# OIL EFFECTS ON TERRESTRIAL PLANTS

# AND SOILS: A REVIEW

Ministry
of the
Environment

ntario

OIL EFFECTS ON TERRESTRIAL PLANTS
AND SOILS:   A REVIEW


BY


R.N. EMERSON
VEGETATION ASSESSMENT UNIT
PHYTOTOXICOLOGY SECTION
AIR RESOURCES BRANCH


ARB-108-83-Phyto

April, 1983

# OIL EFFECTS ON TERRESTRIAL PLANTS

# AND SOILS: A REVIEW

I        *Introduction*

        *The following is a summary of a literature review on oil
effects on vegetation and soil with emphasis on the state-of-the-art
with respect to reclaiming oil polluted surface soils in temperate
climates.   The search revealed several papers and reviews on the
topic.    This review emphasizes the literature summaries and
research by W.B. McGill and coworkers at the University of Alberta,
who have published extensively on oil effects on terrestrial habitats.
Much of the information in the section on* Oil Characterization and
Refining Processes *was exerpted directly from Frankenburger and
Johanson (1982).  The sections on* Toxicity of Different Types of Oils
*and* Oil Fractions *and* Effects on Plant Processes *had been
thoroughly summarized earlier by Hutchinson and Hellebust (1974)
and were extracted directly from that report.*


II       **Oil Characterization and Refining Processes**

        *Oil is a 'catch-all' term representing a wide variety of
crude and refined oils.   Crude oils vary widely in their chemical
composition, consisting of both hydrocarbon and nonhydrocarbon
components.   The hydrocarbon fraction consists of normal alkanes
(saturated, straight-chain alkanes - N-paraffins); branched alkanes
(iso-paraffins); cyclo-alkanes (napthenes); alkanes (unsaturated chain
compounds); napthenic acids (alicyclic compounds with an associated
carboxylic and functional group); aromatic compounds (such as
benzene, toluene, phenol, xylene, and catechol) and asphaltenes.
The asphaltenes are more poorly defined, but consist of complex
ring structures (heterocyclic in nature) and a mixture of polar*

compounds including sulfoxides, guinolines, carbazoles, pyridines, amides, phenolic acid, carboxylic acid, ketones, esters, and porphyrins. The non hydrocarbon class of crude oil includes several inorganics in the form of nitrogen, sulfur, phosphorus, and trace elements such as vanadium and nickel. Several other elements including arsenic, calcium, cobalt, chlorine, chromium, copper, fluorine, iron, lead, manganese, potassium and sodium also have been detected in petroleum (Kacmarek et al, 1981).

The refining of petroleum involves the fractionation of crude oil to the isolated finished products by desalting, dehydrating, heating, distilling, blending and chemically modifying the oil. The crude is distilled and separated into as many as 40 narrow-boiling-range cuts (Kalchevsky and Peters, 1960). The refined product is formed by blending the yields and qualities of these cuts. Based on the refining process, the hydrocarbon constituents will appear in different percentages for various commercial products. With increasing temperature, the percentage of aromatic compounds in the refined product increases while the percentage of normal and branched paraffinic compounds generally decreases. Some of the refined products of crude oil include gasoline, kerosene (fuel oil No. 1), diesel fuel (fuel oil No. 2), and motor oil.

Gasoline is a complex mixture of up to 400 individual components of hydrocarbons as determined by gas chromatography - mass spectrometry techniques (Whittemore, 1979). Virgin gasoline is a volatile liquid containing approximately 50% N-paraffins, 40% cyclic alkanes, and 10% aromatics (Curl and O'Connell, 1977). Alkanes (olefins) also may be found in gasoline if subjected to severe catalytic cracking conditions. Gasoline additives include: tetraethyllead, an effective anti-knock agent yielding lead oxide (PbO) when decomposed; oxidation inhibitors to prevent gum

formation; rust inhibitors to reduce corrosion; and detergents to prevent deposits from building in the automobile carburetor (Larson and Larson, 1960; Hell and Moxey, 1960; Gruse, 1967).

Kerosene is a pale yellow oily liquid composed of approximately 35% N-paraffins, 60% cyclic alkanes, and 15% aromatics (Curl and O'Connell, 1977).

Diesel fuels are blended from both distilled and catalytically cracked fractions. It is a yellow viscous liquid consisting of approximately 30% N-paraffins, 45% cyclic alkanes, and 25% aromatics (Curl and O'Connell, 1977).

Motor oil consists of the more viscous portion of crude after the gas, oil and lighter fractions have been removed by distillation (James, 1960). The paraffinic crudes, rich in wax-free saturates and monoaromatics, are desired for production of motor oils to obtain certain viscometric properties and thermal stability. In refining, vacuum distillation removes the desired hydrocarbon from asphaltic material of the crude residuum (Nelson, 1958). The distilled fractions are extracted with solvents such as furfural, cresylic acid, phenol, sulfur dioxide, chlorex, and nitrobenzene, which remove the polyaromatic and hetero compounds to improve the viscosity index (viscosity-temperature characteristics) and stability of the oil. These solvents must be removed from the oil after extraction, but trace amounts would be expected to remain. Dewaxing also is required for the production of motor oil to remove high-melting paraffins.

Most motor oils are multigrade oils supplemented with additives to improve the viscosity index thereby increasing shear strength. Some of these additives include: viscosity-index improvers, antioxidants, pour-point depressants, extreme pressure

additives, antiwear and friction-reducing additives, and dispersants (Zuidema, 1959; James, 1960). The viscosity-index improvers, such as polybutenes and copolymers of polymethacrylates, break the rapid fall in viscosity with increasing temperature. Antioxidants are added to maintain a longer service life and prevent oxidation of the oil by atmospheric $O_2$, with less subsequent formation of acids and sludges that interfere with the primary function of the lubricant. Some of the common antioxidants used in engine oils include amines (phenyl-o-naphthylamine), metal phenates (alkali-earth salts of phenol disulfides), and Zn salts of thiophosphates and carbamates. Pour-point depressants such as metallic soaps, condensation products of chlorinated wax and alkyl naphthalenes or phenols, and polymethacrylates increase the fluidity of motor oil at low temperatures. Various S and Cl compounds are used as extreme pressure additives. Antiwear and friction-reducing additives such as alkaline-earth phenates are added to neutralize any acids that may have formed from the condensation of gaseous combustion products in cold weather. The most commonly used dispersants to prevent deposition of lacquers and sludges on engine parts are sulfonic acids, phenates, salicylates, thiophosphates, and oxidized olefinphosphorus pentasulfide. Polymeric additives (e.g. lauryl methacrylate and vinyl pyrrolidone) are also used for dispersancy and are superior to the alkaline-earth salts at low temperatures. The addition of these various chemicals to motor oil or any refined petroleum product may improve its physical properties and performance.

III     **Toxicity of Different Types of Oils and Oil Fractions**

The following information has been exerpted directly from Hutchinson and Hellebust (1974).

"From a number of studies on the toxicity of crude oil components on plants and animals it may be concluded that the aromatic fraction is most toxic, followed by olefins, napthenes and the paraffins being the least toxic (Crafts and Reiber, 1948; Havis, et al, 1950; Leonard and Harris, 1952; Baker, 1971; Ottway, 1971). The smaller members of the paraffins series, e.g. octane and decane are very toxic, while dodecane and higher paraffins are nearly non-toxic. However, the low molecular weight members of the paraffins are also most volatile. Methyl substitution of aromatic compounds increases their toxicity (Currier, 1951; Malina, 1964), but also decreases their solubility in water and volatility. Toxicity can therefore be inversely correlated with water solubility. According to Currier (1951), monocyclic aromatics cause acute injury to plants, while polycyclic aromatics cause chronic injury. Some of the polycyclic aromatics in crude oil, e.g. 3,4-benzopyrene, 1, 2-benzanthracene and alkylbenzanthracenes (Carruthers et al, 1967; Graef and Winter, 1968) are known carcinogens (Kennaway, 1924; Badger, 1948; Dr. D.L. Woodhouse, University of Birmingham, private communication cited by Carruthers et al, 1967; Eckardt, 1967)."

"Several other substituted (oxygen or nitrogen containing) aromatic compounds in crude oil are also quite toxic to organisms, and are particularly dangerous because of relatively high solubilities in water; e.g. cresols, xylenols, naphthols, quinolene and pyridines and derivatives of such compounds (Speers and Whitehead, 1969). Toxic oxygen-containing derivatives with high water-solubilities may also be formed as intermediate compounds of microbial degradation, e.g. alkanoic acids, phenols, and aromatic acids (Zobell, 1950; Treccani, 1965; Walker et al, 1973). However, these intermediate degradation products are rapidly further degraded to $CO_2$ and $H_2O$ by a variety of microbial species if

*sufficient oxygen is present (Zobell, 1962). Oil' components may also increase in toxicity by being exposed to direct sunlight through the formation of olefinic derivatives, peroxides and acids (Van Overbeek and Blondeau, 1954). These photochemical conversions are catalyzed by trace elements such as vanadium - a common crude oil constituent - and take place most readily when UV radiation is present. (Frank, 1950; Nelson-Smith, 1970)."*

*"From the above considerations of comparative toxicities of oil components, it may be assumed that the toxicity of a particular crude oil will depend on its -content of aromatic compounds of oxygenated derivatives of aromatic, and to a lesser extent, of aliphatic compounds. While the low-molecular weight paraffins are quite toxic to various organisms, they are also rapidly lost through evaporation and ready microbial degradation. Following an oil spill, the toxicity of the oil can be expected to decrease due to evaporation and microbial degradation of low-molecular weight straight-chain alkanes, and low-molecular weight aromatics. Approximately 1/3 of the total oil may disappear from the scene of the spill through evaporation within days (Brunnock et al, 1968; Mackay et al;, 1972). On the other hand, new toxic components may be formed through photo-oxidation processes, which may be particularly significant if the oil contains high levels of catalytic trace elements such as vanadium and if the site of the spill is exposed to direct sunlight with a high UV component for extended periods of time. Rapid microbial degradation of oil components may initially cause formation of toxic intermediates, but, in general, the presence or induction of a suitable microflora, and a ready access of oxygen is obviously the key factor in breaking down residual oil components and reducing the level and toxicity of oil pollution at a spill site. Although most oil components appear to be degraded by at least some microorganisms, the high molecular-weight branched hydrocarbons and polycyclic aromatic components*

are broken down quite slowly (Treccani, 1965; Gunkel, 1968), and it is possible that crude oil is not entirely biodegradable (Floodgate, 1972). The residual, asphalt-like (oil lumps, or tarballs) crude oil material left behind following extended evaporation and microbial degradation of crude oil appears to be relatively non-toxic, but obviously is aesthetically displeasing. However, Blumer (1971), showed that tar-balls found in the marine environment, resulting from extended weathering, still contained nearly the full range of hydrocarbons of the original crude oil, extending in boiling point as low as $212^{o}F$. These components are presumably "trapped" in the oil lumps. Furthermore, the high-molecular weight aromatic compounds present in high concentrations in weathered crude oil material -while not acutely toxic to organisms - contain potentially carcinogenic components (Blumer, 1971), and may therefore constitute a public health hazard. However, little factual information is available about the actual threat of these compounds (Cowell, 1971)."

IV     **_Effect of Oil on Plants_**

1. _Plant Processes_

The following summary on the effects of oil on plant processes has been selected directly from the work of Hutchinson and Hellebust (1974).

"A number of physiological processes in plants, such as transpiration, (consistently reduced due to physical interference), respiration (reduced or increased by oil), photosynthesis (consistently reduced), and translocation (inhibition), are affected adversely by oil contamination (Baker, 1971)."

"Crude oil readily adhers to and spreads as a thin film on most plant surfaces. Penetration of oil from the surface into plant tissues may take place only as long as there is free oil on the surface (Rohrbaugh, 1941). The rate and extent of penetration is affected by quality and thickness of cuticle, number of stomata, and also depends on oil type, particularly surface tension and viscosity of the oil (Knight et al, 1929, Minshall and Helson, 1949). Plants with heavy cuticles and few stomata are resistant. Oil, after penetrating through stomata or cuticle appears to move within plant tissues through intercellular spaces rather than along vascular tissues (Knight et al, 1929; Young, 1935; Laville, 1963). Oil may further penetrate into individual cells after passing through cell walls and plasma membranes. According to Lewis (1945), the outer walls of mesophyll cells are lipophyllic, which should facilitate oil penetration, but cell walls are normally considered saturated with water which should inhibit passage of oil (Young, 1935). Van Overbeek and Blondeau (1954) suggest that hydrocarbons dissolve in the plasma membrane and make it more permeable to a variety of substances by displacing membrane lipid constituents. Boyles (1967) has demonstrated the disruption of membrane in onion epidermis by n-decane."


2. *Plant Communities*

Oil spills on land can result in direct adverse effects to contacted vegetation. It has been known for some time that oils have herbicidal properties. Any direct toxic effects on plants, notably herbaceous vascular plants, usually are quite distinct. Leaves may display partial injury such as chlorotic or necrotic lesions or become entirely necrotic and prematurely abscise (Ginsburgh, 1931). Some indirect effects on foliage also have been

noted. Hutchinson and Hellebust (1974) observed that five weeks after a crude oil spill regrowth leaves (from previously dormant lateral buds that were stimulated to break dormancy by the oil-induced death of the apical bud) of several species native to Alaska, had very large surface areas (gigantism) relative to control leaves of the same species. They further reported, that the leaves of Ledium palustre had thin cuticles and the tomentose red hairs on the leaf underside which are usually characteristic of this species were absent.

Plant roots also can be directly or indirectly affected by the presence of oil in soil. McCown and Deneke (1973) observed that roots of spruce seedlings growing in pots after the surface soil was treated with crude oil were brown and injured. They also reported that roots of dandelion seedlings were severely injured and death resulted after crude oil was applied to the pots in which they were growing. Root injury also can be related to intermediate compounds - alkanoic acids, phenols and aromatic acids - which can potentially form when oil is biodegraded by microorganisms in soil (Hutchinson and Hellebust, 1974). Soil microorganisms also can deplete important soil nutrients such as nitrogen and thus inhibit root/plant growth (Ellis and Adams, 1961; Volk, 1980; McGill, 1980). In addition, oil contaminated soil may become anearobic and reducing conditions can result in increased solubilities of iron (Fe) and manganese (Mn) to the extent that these potentially phytotoxic elements are absorbed by roots/plants (Gidden, 1976; Volk, 1980). Garner (1971) attributed the deterioration and death of trees and ornamentals to toxicity by sulfides and excess manganese brought about by the anaerobic soil atmosphere created by leaching natural gas displacing the soil air. High oil concentrations in soil not only reduce the amount of water and oxygen available for plant growth (Schwendinger, 1968; McGill, 1980) but also can interfere with soil-

plant-water relations through direct physical contact (coating of root tissues) thereby adversely affecting plant growth (Baker, 1971).

Most researchers who have published on the effects on plants growing in oil contaminated soil have reported mainly symptoms similar to those associated with water stress and nutrient deficiencies - wilting, stunted growth and discoloured (chlorotic or yellow) leaves - as opposed to any direct oil toxicity (Ellis and Adams, 1961; Schwendinger, 1968; Rowell, 1975; Udo and Fayemi, 1975; Giddens, 1976; Raymond et al, 1976; Watts et al, 1982).

Plant parts other than leaves and roots also can be affected. Baker (1971) found that crude oil applied to salt marsh plants during flower bud formation reduced flowering and adversely affected seed production. Blankenship and Larson (1978) who applied a water extract of crude oil to radish plants found that the phenols, carbonyl compounds and carboxylic acids they detected in the extract also inhibited flowering. Other potentially toxic substances which have been detected in water extracts of petroleum products include napthalenes, ketones, indoles and anilines (Boylan and Tripp, 1971; Anderson et al, 1974; Guard et al, 1975; Winter et al, 1977)

Oil application to fruit bearing plants also can potentially result in early blooming, retardation or hastening of the ripening process, premature fruit drop, and reduced fruit quality (Ginsburgh, 1931).

Inhibited seed germination in oil contaminated soil also can be directly or indirectly related to the presence of oil in soil. Plice (1948) attributed poor seed germination to the penetrating power of the volatile fraction of oil. He reported that in contact

*with a seed, oil would enter the seed coat and readily kill the embryo. Baker (1971) reported that apart from any direct toxic effects an oil coating on seeds prevents normal water and oxygen entry. Seed germination also can be indirectly hindered by unfavourable soil conditions such as surface crusts and droughty soil conditions related to soil being contaminated with oil.*

*Oil spills on terrestrial environments can drastically affect a plant community. Sensitive species may become extinct and tolerant species dominate. Overall plant cover can be reduced and some areas may remain barren. In severe spills, a plant community can be drastically altered or eliminated and the affected area(s) may remain unproductive for several years if no attempt is made to reclaim the site (Freedman and Hutchinson, 1976; Kinako, 1981). Kinako (1981) studied the short term effects of a relatively low level of crude oil (11 $l/m^2$) on species numbers and productivity of a simple grass-herb community in Nigeria. He reported that the spillage had a drastic effect on the simple ecosystem and especially on the component herbaceous species. In contrast rhizomatous perennial species were less severely affected. At least 50% of the species in the affected habitats became extinct following the oil application and the total loss in forage production for a period of six months at the polluted sites was as high as 74%. Other researchers also have observed drastic effects on plant communities following oil spills (Odu, 1972; Freedman and Hutchinson, 1976).*

*Oil spills also can contribute indirectly to other aspects of habitat deterioration such as sheet erosion (Kinako, 1981). It is generally accepted that lack of vegetation cover, and disrupted soil structure and reduced moisture holding capacity of oil polluted soil all can contribute to erosion.*

3. _Plant-Oil Interactions_

  _Schwendinger (1968) in summarizing the oil work up to 1968 estimated the critical level at which oil begins to damage plants at about 1 kg per square meter. However, he felt that this was a conservative estimate and underscored the fact that the 'critical' level had not been well established. In this regard he conducted germination tests with oat seeds in loamy-sand contaminated with various amounts of a paraffin-rich crude oil. Based on this and other exploratory crop work, he concluded that about 3% by weight was the 'critical' oil content of the soil under which plants will continue to grow without showing severe symptoms of damage. This value was in good agreement with his earlier estimate._

  _The more recent work by Rowell (1975) who examined germination of oat seeds in sandy Alberta soil to which a paraffinic crude oil had been applied at rates up to 8% (w/w) also supports this estimate. He observed that seed germination was unaffected by oil contents in soil up to and including 4% and that there was no germination at the higher rate (8%). In addition, Mitchell et al (1979), in greenhouse studies with oiled, fertilized, silt-loam, mineral soil removed from a field in Alaska four years after crude oil was applied at 10 and 20 $l/m^2$ found that residual oil levels under 7.5% allowed germination of barley and brome seeds but reduced shoot heights, whereas residual oil contents of 13.5% in the soil completely inhibited seed germination. The work by Schwendinger (1968), Rowell (1975) and Mitchell et al (1979) indicates that seeds can tolerate fairly high levels of oil pollution in soil. However, Rowell (1975) and Mitchell et al (1979) only examined the effects of oil on germination and seedling development. Hence the oil concentrations they suggested as being uninhibitory to seed_

growth cannot be considered as safe levels for plant growth since adverse effects may have developed had the test plants been grown to maturity.

Some of the initial work on interactions between plants and oil were conducted by Carr (1919) whose work was not included in the summary by Schwendinger (1968). Carr (1919) applied crude petroleum to soils at rates up to 4.0% by weight and observed that the growth of soybean plants was markedly reduced at oil applications above 1%. The literature since 1968 also suggests that oil levels in soil much lower than the 3% critical level recommended by Schwendinger (1968) can adversely affect plant growth. Udo and Fayemi (1976) determined the yield of maize planted in Nigerian sand treated with different amounts of crude oil and found that a 1.1% oil level was sufficient to cause a 30% reduction in yield. In addition, based on the work by Raymond et al (1976) who applied six different oils (used crankcase oil from cars, used crankcase oils from trucks, an Arabian heavy crude oil, a coastal mix crude oil, home heating oil No. 2 and a residual fuel oil No. 6) at a single rate of 11.9 $m^3/_{4x10^3 m^2}$ to three geographically different plots which were seeded with radish, turnip, and beans about nine months after the oil treatment, it was apparent that residual oil levels much lower than 3% could adversely affect plant growth. The attached table which was extracted from their report was revised to include the approximate oil content of the soils at time of planting. This table indicates that a level of crude oil as low as 0.4% in a sandy loam soil inhibited the growth of turnip plants. This level was only about 4 times higher than the corresponding background level (0.09%). Also the work by Dejong (1980) who planted oats on heavy clay soil contaminated with crude oil suggested that oil levels less than 0.25% in soil could drastically reduce oat yields. However, he

reported that due to the non-uniform distribution of the oil in the soil that average oil levels much higher than those detected would occur in the root zone.

Based on the work by McGill (1978) and coworkers in Alberta it has been concluded that if an oil spill is extremely light, (less than 1% oil by weight in the plow depth) there will be essentially no direct toxicity to plants. He further stated that serious problems begin to develop in plants when the oil concentration in soil increases above 2%. In severe oil spills the concentration can be about 10% by weight. The conclusions drawn by Carr (1919) and McGill (1978) appear to be in fairly good agreement and based on the literature it would appear that the 3% safe level recommended by Schwendinger (1968) is much too high to assure protection of all plants. The work by Raymond et al (1976) and Dejong (1980) indicate that oil levels in soil even lower than the 1% critical level suggested by Carr (1919) and McGill (1978) is too high for some plants.

Low oil concentrations in soil also have been found to have a stimulatory effect on plant growth. Carr (1919) found that 0.75% crude oil improved the growth of soybeans and increased root nodule development. Nagata and Muramatsic (1968) observed that late application of 0.5 ml heavy oil per 3.5 kg soil stimulated growth of rice. Baker (1971) also observed some growth stimulation of salt marsh grasses following treatment of Marsh soil with weathered kuwait crude oil. Researchers in the USSR (Guseinov and Asodov, 1958; Huseinov, 1960) also have found petroleum derived products to stimulate growth of field crops. The main agents responsible were considered to be petroleum auxins (napthenic acids) and part of the beneficial effect also was attributed to associated micronutrients. Better growth of plants after an oil spill site has

recovered also has been reported (Ellis and Adams, 1961; Giddens, 1976). This response likely is attributed to the beneficial effects of oil on soil: improved soil structure, increased organic matter content, improved moisture holding capacity, and increased fertility (Plice, 1948; Hubbard - see file).

Table 13 from Raymond et al, 1976

| | Markus Hook (radishes) (silt loam) | | | Tulsa (Turnips) (sandy loam) | | | Plant response in control and treated plots[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Corpus Christi (clay loam) | | |
| | | S | C | | S | C | Plant | | S | C |
| Control | (0.04)[c] | ++++ | N | (0.09)[c] | ++++ | N | Turnips | (0.05)[c] | ++++ | N |
| | | | | | | | Beans | | +++ | N |
| CC | (1.6) | - | - | (0.6) | - | - | Turnips | (1.5) | +++ | S |
| | | | | | | | Beans | | +++ | M |
| DC | (1.3) | - | - | (0.7) | - | - | Turnips | (1.6) | +++ | M-Y |
| | | | | | | | Beans | | +++ | M-Y |
| HAC | (1.2) | ++++ | S | (0.5) | - | - | Turnips | (1.0) | ++ | S |
| | | | | | | | Beans | | +++ | S |
| CLC | (2.0) | - | - | (0.4) | - | - | Turnips | (1.2) | ++ | M |
| | | | | | | | Beans | | + | VS-Y |
| No. 2 | (0.5) | - | - | (0.05) | ++++ | S | Turnips | (0.3) | +++ | N |
| | | | | | | | Beans | | +++ | N-Y |
| No. 6 | (2.4) | ++++ | S | (1.6) | ++++ | M | Turnips | (1.2) | - | |
| | | | | | | | Beans | | +++ | M-Y |

[a] S, stand; C, condition; N, normal; M, medium; S, small; Y, yellow, PG, pale green. Symbols: ++++, normal; +++, several; ++, few; +, very few; -, none.

[b] CC, crankcase oil from cars; DC, crankcase oil from trucks; HAC, Arabian Heavy crude oil; CLC, Coastal Mix crude oil; No. 2, home heating oil No. 2; No. 6, residual fuel oil No. 6.

[c] Approximate oil content in soil at time of planting (9 months after oil applied to soil) expressed in percentage (%). In original tables, concentrations were expressed in g/kg (dry wt) - see tables 3, 4 and 5 of Raymond et al, 1976

4. _Species Tolerance_

Researchers are in good agreement that plant tolerance to oil is species dependent but the research in this area is scant. Many generalizations which have been made with respect to oil tolerant species have been based on field observations following an oil spill. Some researchers have assessed the ability of a plant species to recover as a means of assessing its tolerance to oil.

Plant species with a thick cuticle and few stomata have been reported to be fairly tolerant (Hutchinson and Hellebust, 1974). The literature also suggests that perennial plants generally are more tolerant than annuals.

Baker (1969), concluded that plants with large underground food reserves in root systems (rhizomes, stolons) are more likely to recover rapidly than plants lacking reserves such as most annuals. Baker (1971) found that in a salt marsh, near Pembroke, Wales, most perennial species sustained little long term damage from crude oil while annuals were severely reduced in numbers. Kinako (1980), also found the effect of crude oil to be more severe on herbaceous species and attributed this to their high degree of succulence coupled with their non rhizomatous habit. He found perennials to be fairly resistant. In addition, Freedman and Hutchinson (1976) found that rhizomatous plants had a high ability to recover after oil spills. Other workers also have found rhizomatous plants to have an advantage over non-rhizomatous species in ability to recover following an oil spill (McCown and Deneke, 1973; Watts et al, 1982).

Vegetable crops such as tomatoes and leaf lettuce which lack underground rhizomes or storage organs generally are considered to be fairly sensitive (Schwendinger, 1968). Lachman (1944) found that members of the family umbelliferae (e.g. parsnip) were fairly tolerant to light oil sprays.

Based on the previous information, fruit crops such as strawberry also should have a high ability to recover following an oil spill.

With respect to cultivated crops such as barley and oats, the work by Toogood (1974) and McGill and Nyborg (1975) in Alberta, indicate that oats are fairly tolerant. Toogood (1974) in studying germination and vegetative growth of several common crops including oats, wheat, barley, rapeseed and flax, planted in oil contaminated soil, found that barley, rapeseed and flax were the most sensitive. He reported that of all the crops tested rapeseed appeared to be the most sensitive with barley and flax next. Based on the literature reviewed, the tolerance of crops such as corn and soybean is not well established.

With respect to grass species, the work by Schwendinger (1968) suggests that hardy grasses such as rye grass are fairly tolerant. McCown and Deneke (1973) also found seedlings of rye grass to be least sensitive compared to spruce and dandelion seedlings in oiled soil. In addition, Watts et al (1982) observed three years after waste oil was applied to a site that crabgrass was the most common species. Crabgrass survives by underground rhizomes and is known to be extremely hardy. The work by McGill and Nyborg (1975) also indicates that grasses such as timothy, brome grass, and reed canary grass, which are used in crop rotations, are fairly tolerant. Sedges also have been found to be fairly tolerant (McGill and Nyborg, 1975; Hutchinson and Hellebust, 1975-76).

Also, there were at least two published studies which indicated that legumes are fairly tolerant (Grummer, 1965; Gudin and Syratt, 1975). Grummer (1965) reported large stands of red clover on an oil spill site. Also, Gudin and Syratt (1975) found that members of the Leguminosae were abundant on soils containing heavy hydrocarbon material, often forming extensive stands and occasionally being the only species present. The following table was exerpted directly from Gudin and Syratt (1975) and shows the main leguminous species that were identified at the fifteen different sites they examined.

## REPRESENTATION OF LEGUMINOSAE AT ALL SITES INVESTIGATED

| Location | Hydrocarbon impregnation | Main leguminous species |
|---|---|---|
| *Natural Hydrocarbon Impregnation* | | |
| West Calder (Scotland) | Bituminous shale | Lotus corniculatus the only plant on one outcrop |
| Chevenay (France) | Bituminous shale | Melilotus altissima (the only species on some exposed bituminous shale outcrops) |
| Manosque (France) | Bituminous shale | Psoralea bituminosa on bituminous horizons |
| Dax (France) | Bituminous sand | Robinia pseudacacia roots penetrating bitumen |
| Lodeve (France) | Bituminous shale | Psoralea bituminosa on bituminous horizons |
| Avejan (France) | Bituminous shale | Psoralea bituminosa on bituminous horizons |

| Location | Hydrocarbon impregnation | Main leguminous species |
|---|---|---|
| St Denis-Catus (France) | Bituminous shale | _Psoralea_ _bituminosa_ on bituminous horizons |
| | _Exploitation Areas_ | |
| Autun (France) | Bituminous shale | _Vleia_ _tetrasperma_ forming extensive stands on unprocessed shale tip |
| Lobsànne (France) | Asphalt dust from mine | _Lotus_ _corniculatus_ forming extensive stands (31% leguminous cover) |
| Avejan (France) | Asphalt dust from mine | _Medicago_ _sativa_ forming extensive stands around asphalt tips |
| | | _Trifolium_ _repens_ abundant on lawn contaminated with lignite dust |
| Severac-le-Chateau (France) | Bituminous shale | _Medicago_ _sativa_ (the only species on an unprocessed shale tip) |
| | _Oil-polluted Areas_ | |
| Grangemouth refinery (Scotland) | Heavy product spill | _Trifolium_ spp. (2) forming extensive stands |
| Llandarcy refinery (Wales) | Mixed residues (in lagoon) | _Trifolium_ _repens_ forming extensive stands on lagoon causeway |

| Location | Hydrocarbon impregnation | Main leguminous species |
|----------|--------------------------|-------------------------|
| Dunkirk refinery (France) | Mixed product spill | _Medicago lupulina_ plus others forming up to 41.5% cover on polluted zone |
| Lavera refinery (France) | Heavy product spill | _Psoralea bituminosa_ on spill |
| | | _Medicago_ spp. forming extensive stands around vacuum distillation plant |

Gudin and Syratt (1975) stated that the relative abundance of members of the Leguminosae on hydrocarbon contaminated sites could be due to the competitive advantage offered by the symbiotic nitrogen-fixing relationship between the Leguminous species and Rhizobium spp. so that Leguminous species are not dependent on available nitrogen for which soil micro-organisms are strongly competing. Their reports indicated that legumes are best for revegetating oil contaminated soil.

McGill and Nyborg (1975) found legumes successful and they will apparently grow in oil contaminated soil about as well as many grasses and possibly better than some. Nevertheless, they reported that there is no proof that they fix nitrogen under these conditions and until this is forthcoming, unqualified support of legumes as best in a reclamation program would be misleading. McGill and Nyborg (1975) tested the following species and assigned a general rating based on their ability to survive.

| Common Name | Scientific Name | Rating |
| --- | --- | --- |
| Oats | _Avena sativa_ | Good |
| Timothy | _Phleum pratense_ | Medium |
| Brome Grass | _Bromus Inermis_ | Medium |
| Reed Canary Grass | _Phalaris arundinacea_ | Good |
| Streambank Wheat grass | _Agropyron riparium_ | Good |
| Creeping Red Fescue | _Festuca rubra_ | Medium |
| Alsike Clover | _Trifolium hydridum_ | Good |
| Willow | _Salix sp._ | Medium |
| Dogwood | _Cornus stolonifera_ | Medium |
| Black Spruce | _Picea mariana_ | Poor |
| White Spruce | _Picea glauca_ | Poor |
| Larch | _Larix laricina_ | Poor |

Also included in that report was a list (shown below) of plants which have been found growing wild in oil contaminated soil.

| Family | Genus and Species | Common Name |
| --- | --- | --- |
| Compositae | _Solidago lepida_ | Goldenrod |
|  | _Sonchus_ | Sow Thistle |

| Family | Genus and Species | Common Name |
|---|---|---|
| | *Bidens cernua* | Beggar-tick |
| | *Senecio* | Ragwort |
| Cornaceae | *Cornus canadensis* | Bunchberry |
| Cyperaceae | *Carex aquatilis* | Sedge |
| | *Eriophorum chamissonis* | Cotton Grass |
| Equisetaceae | *Equisetum* | Horse Tail |
| Ericaceae | *Vaccinium* | Blueberry |
| | *Ledum groenlandicum* | Labrador Tea |
| Gentianaceae | *Menyanthis trifoliata* | Buck-bean |
| Graminae | *Phalaris arundinacea* | Reed Canary Grass |
| Agrostideae | *Agrostis* | Bent Grass |
| Festuceae | *Festuca* | Fescue |
| Pamicoideae Hordeum | *Agropyron smithii* | Western Wheat Grass |
| Juncaceae | *Juncus* | Rush |
| Leguminoseae | *Melilotus alba* | Sweet Clover |
| | *Trifolium hybridum* | Alsike Clover |
| Labiatae | *Galeopsis tetrahit* | Hemp-Nettle |
| Onagraceae | *Epilobium augustifolium* | Fireweed |
| Ranunculaceae | *Ranunculus* | Buttercup |
| Rubiaceae | *Galium boreale* | Northern Bedstraw |
| Salicaceae | *Salix* | Willow |
| Saxifragaceae | *Heuchera* | Alumroot |
| Umbelliferae | *Sanicula* | Snakeroot |

Other workers also have found perennial weeds to have a fairly high ability to establish on oil spill sites (Toogood, 1974; Rowell, 1975; Mitchell and Loynachan, 1979).

With respect to tree species, the report by McGill and Nyborg (1975) and the work by Hutchinson and Freedman (1978) indicate that members of the coniferous family (black and white spruce and larch) have a low tolerance to oil and poor ability to survive after an oil spill. Willow and dogwood were rated as medium in ability to survive by McGill and Nyborg (1975).

Based on the work by Baker (1971), Hutchinson and Hellebust (1974), and Freedman and Hutchinson (1976), it would appear that plants, notably herbaceous vascular plants, are more susceptible to injury by oil spills that occur during the summer.

## V. *Effects of Oil on Soil*

### 1. *Migration*

Following a spill, oil usually will penetrate the surface soil and migrate vertically downward into the subsoil under the influence of gravity, capillary and pressure forces (Dietz, 1972; Raisbeck and Mohtadi, 1974; Hubbard - see file; Vanloocke et al, 1975).

The degree and extent of vertical oil migration into the soil will depend mainly on the soil type and type and amount of oil spilled (Harris - see file; McGill, 1980).

Under field conditions, it is common for the soil to be heterogeneous and consist of layers of different permeability (Hubbard - see file). If the oil moves downward in the soil and reaches a nearly impermeable layer such as clay, lateral spreading on top the clay layer may occur (Hubbard - see file). According to Dietz (1972), several layers common in soil may allow hydrocarbon molecules to penetrate the crystalline lattice of their layered structure and this causes a swelling effect in the clay fraction of the soil making it impermeable to both oil and water.

Depending on the spill site, the oil or water soluble constituents may migrate as deep as the water table and form an oil lens or oil pancake above it (Vanloocke et al, 1975). According to Vanloocke et al (1975) less than 1 ppm of oil products is sufficient to give water a foul odour and render it unpotable.

If a high volume of oil is spilled and cannot penetrate the surface soil to any marked extent, it may flow into low areas or drainage channels of the area and eventually pollute the nearest stream, river or reservoir (Harris - see file).

According to Hubbard (see file), very viscous oils, such as heavy fuel oil and many crude oils hardly penetrate into soil. In loam, silty clay or clay the permeability for oil is at least two orders of magnitude lower than in fine sand; hence the penetration of oil in such soils can practically be neglected. Other researchers also have reported very little penetration by heavy oil into soil (Kincannon, 1972; Rowell, 1975; Raymond et al, 1976; Vanloocke et al, 1979). Thus, based on these reports, light oils likely would have the greatest chance of reaching and contaminating the water table particularly if it was close to surface.

## 2. Physical Effects

*The moisture content of a soil following oil application will either increase or decrease, depending on the site. McGill (1980) reported that soil will 'wet-up' in poorly drained low areas where oil will naturally pool whereas on slopes the movement of oil over the soil surface will result in a non-wettable dry soil. Usually well aerated contaminated soil will have a tendency to dry out and be more prone to soil erosion (McGill, 1978; Rowell, 1975; Loynachan, 1979).*

*Different authors have reported that oil treated soils generally 'wet-up' more slowly in comparison to non-polluted soils (Toogood et al, 1977; Volk, 1980). Volk (1980) attributed this to the non-polar characteristics of oil. Watts et al (1982) reported that spills of certain types of oil, especially those with high viscosity, may result in poor or restricted water infiltration and a concomitant loss in wetting.*

*The application of oil to soil also can create a soil crust, further restricting the infiltration of water and oxygen into the soil profile (McGill and Nyborg, 1975; Volk, 1980).*

*Some workers have observed soil dispersion and disentigration of soil structure after application of oil (Ellis and Adams, 1961; Rowell, 1975) whereas others have observed aggregation of oil-treated soil (Giddens, 1976; Raymond et al, 1976).*

Udo and Fayemi (1975) and others (Ellis and Adams, 1961; Giddens, 1976) have observed that after the oil is decomposed and converted to normal soil organic matter, the soil structure is improved.

## 3. Chemical Effects

One of the major effects of oil on soil is the inhibition of nitrification of ammonium-N to nitrate-N (Ellis and Adams; 1961; Schwendinger, 1968; ODU, 1972; Udo and Fayemi, 1975; McGill, 1977).

Extractable phosphorus and potassium levels also may become depressed (Udo and Fayemi, 1975; Loynachan, 1979) or may increase (Ellis and Adams, 1961; Watts et al, 1982) in soil following oil contamination.

It is generally accepted that available soil nutrients, notably nitrogen, are immobilized by soil microorganisms following oil application (Ellis and Adams, 1961; Schwendinger, 1968; Giddens, 1976; McGill, 1977). Phosphorus is usually fairly immobile in soil.

According to Ellis and Adams (1961), the increase in phosphorus could be explained on the basis of a more fovourable pH and the fact that some phosphorus could be brought into solution by reducing conditions that make iron phosphates more soluble. Volk (1980) reported that the increase in potassium found after oil addition to soil likely was related to the release of potassium initially present in the oil.

There usually is a high demand for oxygen by soil microorganisms following oil addition to soil and oxygen levels in oil contaminated soil may become depleted, contributing to anaerobic or reducing conditions (Volk, 1980).

Several authors have reported that anaerobic or reducing conditions also can result in increased solubilities of manganese and iron in oil contaminated soil (Ellis and Adams, 1961; Schwendinger, 1968; McGill, 1977).

An increase in total nitrogen, organic carbon and organic matter also has been reported (Ellis and Adams, 1961; Watts et al, 1982) as has an increase in the C:N ratio of oil treated soil (Udo and Fayemi, 1975).

Some authors also have reported that the soil pH tends to shift to neutral values after hydrocarbon addition to both acidic and alkaline soils (Vanloocke et al, 1975).

In addition, it has been reported that oil spills normally increase soil temperature from $1^{\circ}$ C to $10^{\circ}$ C (McGill, 1980) and this is believed to be related to solar warming associated with the darker colour of the oiled soil (Johnston, 1970; Raymond et al 1976) and to a lack of vegetative cover which would normally shade the soil.

## 4. Non-Biological Degradation Processes

Based on the literature, it appears that volatilization is the main non-biological mechanism by which oil in soils is lost.

Schwendinger (1968) reported volatilization losses as high as 40% from oil polluted soil. Experiments in Alberta, where Redwater oil was added to field soil indicated that about 30% of the added oil was lost by volatilization (Rowell, 1975). According to McGill (1977) volatilization losses may amount to as much as 20 to 40% of the fresh weight of a light oil. McGill (1977) further states "This process is relatively rapid if the soil is aerated and can be expected to be complete within one month at $20^{o}$ C from a well aerated soil where oil contamination has been restricted to the top 0-10 cm. In soil where oil has penetrated to 30 cm or more, losses by volatilization would be slow unless the soil were tilled or aerated by forced air pipes".

Leaching and photo-oxidation also are possible mechanisms for oil loss. However, the literature suggest that the amount of oil removal from soil by either of these mechanisms is low in comparison to volatilization and microbial degradation (Volk, 1980; McGill, 1977; Dibble and Bartha, 1979).

Dibble and Bartha (1979) estimated the quantity of organic carbon removed from the soil by leaching to be between 1 and 2 percent of the hydrocarbon removed through biodegradation.

With respect to photo-oxidation, since following a spill much of the oil would end up beneath the soil surface and be unexposed to direct sunlight, it is likely that losses due to this process also are extremely low (McGill, 1977).

## 5. Biological Degradation Processes

*Oxidation by soil microorganisms is the principal mechanism by which oil in soil is biodegraded (Schwendinger, 1968; McGill, 1977).*

*It has been reported that many genera of bacteria, actinomycetes and fungi present in the soil can metabolize hydrocarbons ranging from light oil through heavy lubricating oils to asphalts and tars (Schwendinger, 1968). Aerobic bacteria and fungi appear to play the more important role in the oil degradation process (Jones and Edington, 1968; Jensen, 1975a; Jenson, 1975b; Vanloocke et al, 1975; Llanos, 1976).*

*Degradation occurs at oil-water interfaces of soil pores where decomposing organisms are located (Vanloocke et al, 1975; McGill, 1980). According to McGill (1980) it is probable that most oily substrates move as an emulsion or in solution to microbes as opposed to microbe movement to oil substrate as there is normally a low number of microbes in most soils and as their movement in soil is restricted.*

*Following an oil spill, the microbial population in the soil will go through a short period of adaptation or lag phase (Rowell, 1975). Vanloocke et al (1975) reported that the lag phase often encountered in soil metabolism upon the application of hydrocarbons was caused by the toxicity of low boiling and aromatic hydrocarbons. The toxicity aspect was further supported by work by Walker et al (1975). Rowell (1975) observed that with most of the Alberta soils he examined the lag time was equivalent to the time required for the active oil degrading microbial populations to grow and synthesize the enzymes required for oil decomposition. He also*

observed after the addition of crude oil (5% w/w) to several mineral soils that there was normally a lag period of 1-3 days before any detectable rise in carbon dioxide production occurred in the soils. On the basis of these reports, it appears that the adaptation time depends to a large extent on the microbial population present in the soil, site and climatic conditions, and the type and amount of oil spilled.

After the microbial population has adapted to the oil, usually microbial numbers and activity increase (Jensen, 1975; Rowell, 1975). Several researchers have demonstrated increases in microbial activity following the addition of oil to soil by measuring either oxygen uptake or carbon dioxide evolution of the oil contaminated soil (Gudin & Syratt, 1975; Rowell, 1975; Watts et al, 1982).

Oil biodegradation in well aerated soil has been found to be closely related to microbial activity. Oil biodegradation in soil usually is fairly rapid in the beginning and then slows down or declines (Jensen, 1975; Dibble & Bartha, 1979; Rowell, 1980).

Oil biodegradation in soil is largely due to aerobic reactions and thus proceeds fastest in well aerated or oxygenated surface soils. In sub soil, anaerobic conditions usually prevail and in soils where oxygen reserves are low oil biodegradation will occur much more slowly (Hubbard - see file). Both the presence of oil in soil and poor drainage can cause anaerobic conditions (McGill, 1980).

Based on laboratory and field studies there is evidence that some constituents of oil are preferentially metabolized by hydrocarbon decomposers and that decomposition rates differ between oil types (Jobson et al, 1972; Rowell, 1975; Raymond et al, 1976; Walker et al, 1976; Walker et al, 1976; Fedorak and Westlake, 1981).

Laboratory studies have revealed that unbranched or normal alkanes (paraffins) are generally the most rapidly metabolized group of compounds of those studied. Within this group, the medium range paraffins ($C_{10}$-$C_{18}$) are the most readily oxidized. The longer chain molecules are so insoluble and difficult to disperse in water that they decompose more slowly. The lighter saturated chain hydrocarbons, which are more soluble than the medium and longer chain molecules, are not metabolized rapidly because their higher water solubility tends to make them sufficiently toxic to inhibit bacterial growth. Aromatic hydrocarbons are even more soluble than lighter paraffins and also tend to be more toxic because of this. Once a population has adapted to them, they degrade rapidly but at a slower rate than unbranched alkanes (Volk, 1980).

Fedorak and Westlake (1981) determined the sequence of microbial degradation for aromatic and saturate components of Prudhoe Bay crude oil applied to soil enriched with nitrogen and phosphorus. They found the susceptibility of aromatic compounds to microbial degradation over an 11 day period to be: $\simeq$ naphthalene 2-methylnaphthalene > 1-methylnaphthalene > dimethylnaphthalenes $\simeq$ dibenzothiophene $\simeq$ phenanthrene > $C_3$-naphthalenes > methylphenanthrenes > $C_2$-phenanthrenes. The n-alkanes and isoprenoids (pristane and phytane) were also extensively degraded during this time.

Based on the preceding data, it appears that oils with a high n-saturate or paraffinic fractions should be degraded faster than those with a high fraction of aromatic compounds.

Some researchers have found this to be so while others have not observed any great difference in decomposition rates between the two fractions.

Rowell (1975) in soil incubation experiments with different crude oils in Alberta soil found that oil decomposition varied with the nature of the oil, with Pembina crude, a paraffin-rich oil being readily degraded. The rate of degradation of a synthetic crude rich in aromatic constituents was slower and that of a Lloydminister crude, a highly viscous asphaltic crude, was slowest.

Raymond et al (1976), in comparing the rates of decomposition of six oils applied to soil at three locations reported that home heating oil No. 2 was biodegraded the fastest and fuel oil No. 6 normally, but not always, the slowest. Biodegradation of car crankcase oil, diesel crankcase oil, heavy Arabian crude and coastal mix crude oil, was intermediate in nature. On the basis of these findings, the authors concluded that the rates of degradation of the paraffinic and aromatic type compounds did not differ greatly. Fedorak and Westlake (1981) provided further evidence in agreement with this conclusion.

Kincannon (1972), in land cultivation studies, found similar decomposition rates between crude oil, bunker C fuel oil and waxy raffinate oil. Franke and Clark (1974) found no difference in soil decomposition rates with either crankcase or vacuum pump oil.

Westlake et al (1974), based on their work with oil in liquid culture, also found that the presence of a normal or high level of n-saturate (paraffinic fraction) components did not confer biodegradability of an oil.

Biodegradation rates for oils high in asphaltic content is low due to their insolubility, low surface area, and heterogeneous nature (Volk, 1980).

In addition, Frankenberger and Johanson (1982), in examining the oxidative state (dehydrogenase activity) of soils treated with crude oil, leaded gasoline, kerosene, diesel fuel and motor oil, concluded that oxidation inhibitors added to fuels can prevent rapid degradation of such oils in soil. This conclusion was based on their data which indicated leaded gasoline and diesel fuel are oxidized at a less rapid rate than crude but somewhat greater than the rates of kerosene and motor oils. Based on this and other reports (Rowell, 1975; Lehtomaki and Niemela, 1975; Raymond et al, 1976), it would appear that light oils generally are biodegraded at a faster rate in soil than heavy viscous oils.

With respect to the effect of the type of oil or oily waste on its decomposition rate in soil in the field, McGill (1980) concluded that properties resulting in inaccessibility to organisms (e.g. high viscosity, insolubility) and a high content of asphaltic material would appear from the information available to retard decomposition the most.

At least two studies have been conducted whereby the investigators have determined the oil concentration in soil at which oil biodegradation is optimal. Jensen (1975) incorporated oily waste into soil at concentrations varying from 0 to 30% (wt/wt). He observed the highest oxygen uptake rate at a concentration of 5%. The total microbial counts increased with oil application to the 5%

level but declined thereafter, supporting the $O_2$ uptake data. Dibble
and Bartha (1979) also applied oily sludge at various rates to soil
and, based on $CO_2$ evolution data, also found that an application
rate of 5% wt/wt oil sludge hydrocarbon to soil resulted in the best
overal biodegradation rates of all hydrocarbon classes (saturated,
aromatic and asphaltic). Their data also indicated that application
rates that are over optimal for a rapid removal of saturated
hydrocarbons favor removal of the aromatic and asphaltic classes.
Their interpretation of this, although speculative, was that the
biodegradation of the higher aromatics and of the asphaltic
compounds, few of which can serve as growth substrates by
themselves, is dependent upon a continued presence of saturated
hydrocarbons to support the cometabolic biodegradation of the
former classes.

## 6. Environmental Factors Affecting Degradation

The effect of environmental factors on oil degradation
in soil was evaluated by McGill (1980) in Alberta and by Dibble and
Bartha (1979) in New Brunswick. Much of this section is based on
their work.

### Organic Matter, Clay Content, Soil Moisture

As organic matter provides a highly adsorptive surface
and has a high wetting capacity its content will influence the
amount of oil retained in the soil. Generally, soils with a high
organic matter content have a greater oil holding capacity than
those with low organic matter content. Organic matter also
provides a supply of nutrients for utilization by soil microbes
(McGill, 1980).

Rowell (1975) examined the effect of organic matter and clay content on the rate of decomposition of oil in eight Alberta soils. The soils varied in organic matter content from 1.7 to 10%. Clay content ranged from 16 to 66% and pH ranged from 5.5 to 7.6 The results of his laboratory tests revealed the fastest rate of oil decomposition in high organic matter soils. In soils with low organic matter contents, microbial decomposition of oil was very slow. With respect to the effect of clay on oil biodegradation, Rowell (1975) observed after incubating the soils for 24 weeks, that reduction in oil content was significantly correlated with clay content. He further stated, "It was thought that microbial metabolism of oil resulted in breakdown products that were non-extractable through their association with clay surfaces in the soil. This appears to be a factor only where the clay content is high relative to the organic matter content or where pH is low and the clay content relatively high." According to McGill (1980), clay content influences the physical properties of soil and, if it is high, may reduce moisture infiltration and aeration and indirectly slow down decomposition. He further stated that tillage operations also may be affected adversely by clay content in excess of 40%.

Soil moisture content, as influenced by organic matter and clay content, also can influence the amount of oil retained by the soil and affect the rate of oil decomposition. It is generally accepted that soil with a high moisture content usually will absorb less oil than dry soil.

Kloke and Sahm (1961) found that soils are able to absorb oil to a maximum of one third of the weight of water held at field capacity. Rowell (1975) indicated that this was a reasonable approximation based on one of his studies where he used a sandy soil

*from Alberta which had been contaminated with a paraffinic crude at rates up to 8% (wt/wt), the field capacity moisture content of the soil being about 15%. He observed at the 8% level that oil was present in the larger soil pores and had a tendency to drain slightly from the soil. At the 4% rate the soil was not quite fully saturated with oil.*

*Based on the literature, it appears that if a soil becomes extremely dry following oil application, biological decomposition processes will not be optimum. On wet sites, the oil degradation process also will be impeded principally due to poor aeration. In addition, McGill and Nyborg (1975) found that wet sites are difficult to manage mechanically and thus create problems in conducting other reclamation operations.*

*With respect to the influence of soil moisture on oil biodegradation, it stands to reason that optimum degradation would occur at soil water potentials at which bacteria and other microbes function well.*

*Based on studies by Wilson and Griffin (1975) concerning water potential and respiration of soil microorganisms in the soil, bacteria appear to function well at soil water potentials of -3 to -5 bars or greater. At -20 bars* <u>*Bactillus*</u> <u>*subtillis*</u> *was only 11% as active as at -3 bars. Fungi were found to be much more tolerant of desiccation than bacteria.*

*Dibble and Bartha (1979), in a laboratory study with oil sludge incorporated into a soil, found oil degradation to be optimal at a soil water holding capacity of 30-90%.*

## Soil pH and Temperature

The influence of soil pH on oil decomposition was evaluated by McGill and Nyborg (1975) who found that oil decomposition was slow under acidic peat soil conditions. Rowell (1975) reported that "under acidic conditions microbial activity is slower and fungi tend to predominate over bacteria. Bacteria are probably the most important group at least in the early stages of oil decomposition and are favoured over fungi by neutral to slightly alkaline pH values." Vanloocke et al (1975) reported that in the neutral pH region (6-7.5) bacteria as well as actinomycetes and fungi can be active. Dibble and Bartha (1979) found that oil sludge biodegradation was optimal at a soil pH of 7.5 to 7.8. Studies conducted in Alberta also indicate that optimal oil biodegradation occurs at a near neutral pH (McGill, 1978; Rowell, 1980).

On the basis of the literature, air temperatures also can influence the rate of oil biodegradation in soils. There is evidence that biodegradation of oil in soils occurs in most climates ranging from hot tropical ones to cold artic regions typical of the Yukon territory (Udo and Fayemi, 1975; Gossen and Parkinson, 1973). According to Rowell (1980), hydrocarbon decomposition may be expected to occur in cold regions in much the same way that it does in warmer environments; however, the rate of decomposition will be slower.

With respect to temperate climates, studies conducted by the University of Alberta (McGill, 1978) and also the work by Dibble and Bartha (1979) have shown that optimal oil biodegradation occurs in soils under air temperatures ranging from about 12 to $30^{\circ}C$ (55 to $85^{\circ}F$).

VI.    **Reclamation of Surface Soils**

1. _Fertilization and Tillage_

Several summaries have outlined remedial procedures for oil-spill site restoration. In temperate climates, fertilization and tillage have received greater attention than other remedial practices (Ellis and Adams, 1961; Schwendinger, 1968; Gudin and Syratt, 1975; McGill, 1977).

The addition of fertilizers to oil contaminated soil replenishes the soil store of nutrients and counteracts deficiencies associated with immobilization of available nutrients by soil microorganisms. Several researchers have observed following the addition of high nitrogen-phosphorous fertilizers to oil contaminated soil that microbial activity or rate of oil biodegradation was enhanced considerably (Jensen, 1975; Rowell, 1975; Gudin and Syratt, 1975; Loynachan, 1978; Dibble and Bartha, 1979).

However, Dibble and Bartha (1979) found no evidence that addition of potassium and micronutrients to oil contaminated soil stimulated hydrocarbon biodegradation under laboratory conditions. The work by Atlas (1977) and Bartha and Atlas (1977) also failed to indicate that oil biodegradation is enhanced by potassium addition to oil polluted soils.

McGill (1977) pointed out that the role of nitrogen in the biological decomposition process is better understood than that for other nutrients.

The following was taken directly from a review by McGill (1978).

*"Nutrient supply becomes one of the main variables to be controlled. How much should be used? The amount needed depends on the amount used in soil decomposition and the amount provided by the soil. A simulation of the system has yielded a few general estimates of potential nitrogen usage. For situations where oil decomposition is likely to be rapid (mean annual air temperature 55 degrees or greater and an oil that is neither extremely volatile such as light fuel oils nor extremely heavy, such as very asphaltic crudes) an estimate of the nitrogen requirements can be made using the following approximation:*

*Pounds of nitrogen needed per acre equals percent oil by weight in top 6 inches times 173, minus 130. In cooler regions (mean annual air temperature less than 50 degrees) a better estimate would be: 1b N needed/acre = (% oil in top 6") (104) - 140. For very asphaltic crudes (e.g. Lloydminster) the following may be used:*

*1b N needed/acre = (% oil in top 6") (59) - 150. As indicated in this formula, up to 2 percent asphaltic crude may be handled by the nitrogen released by the soil.*

*These approximations assume about 1.5 percent organic matter in the soil. Subtract about 100 pounds of nitrogen per acre for every 1.5 percent organic matter in excess of this level. Remember this calculation will provide only an initial estimate of what to expect. The*

*exact amount needed will be determined during site monitoring. The longer a site is given for restoration the smaller becomes the amount of nitrogen needed. Added nutrients only hasten the process - they will likely not promote any biological process that would not have occurred in their absence unless the soil has absolutely no nutrients, which is highly unlikely.*

*Phosphorus should normally be applied with the nitrogen at a ratio of 1 part phosphorus for every 3 to 5 parts nitrogen. The need for potassium and sulfur will vary with local soil conditions and the type of oil. Many oils contain enough sulfur so that adding more is not necessary. If the soil is low in potassium, it could be included at a ratio of one part potassium per 10 parts nitrogen.*

*Nutrient additions should be spread out. Additions of more than 200 pounds per acre of nitrogen at one time are not recommended because this may lead to salinity problems and/or ammonia volatilization or toxicity problems.*

*The type of fertilizer to use deserves some consideration. Ammonium nitrate has been found effective but up to 50 to 80 percent losses of the nitrate nitrogen may occur in an oil spill situation. Urea is good, but if a crop is seeded concurrently, the lack of nitrification in many oil spill situations and resultant high ammonia levels may be detrimental to plant growth. Anhydrous ammonia suffers the same disadvantages. Ammonium sulfate supplies sulfur in addition to nitrogen but is not recommended for high application rates, because of its tendency to acidify soil."*

*Lysimeter studies by Dibble and Bartha (1979) also indicate that nitrogen losses following fertilizer addition to oil polluted soil can be prevented and oil biodegradation can be effectively stimulated by using a slow release fertilizer. The slow release fertilizer used in the experiment was urea formaldehyde.*

*In reclaiming oil spill sites, according to McGill (1978), fertilizers should be broadcast and tilled thoroughly into the soil. The main benefit of tillage is that it breaks up the soil crust, increasing the soil oxygen supply (McGill, 1980). Rowell (1975) has found that even minimal tillage will enhance oil biodegradation but, according to Mitchell et al (1979), frequent tilling likely would be more effective than a single tilling in enhancing the process. However, excesive tillage should be avoided to prevent drying out of the soil and serious erosion losses (McGill, 1978; Mitchell et al, 1979).*

*Plice (1948) reported that oil damaged soils are best reclaimed by cultivation after the petroleum has "hardened" to the extent that the soil will scour a ploughshare. Mitchell et al (1979) also recommended delaying tillage until sufficient time has lapsed for adequate volatilization to ocur, thus permitting the loss of volatile toxic fractions before incorporating the contaminant deeper in the soil profile. They also recommended that in cases where tilling may produce serious soil erosion, that tillage be delayed until there are reasonable assurances of planting success.*

*Toogood and McGill (1977) found that agricultural soils in Alberta could be reclaimed in one year if contamination was light*

*(2.5% or less by dry weight of the plow layer depth) with proper fertilization and tillage. Also, McGill and Nyborg (1975) reported that tillage and fertilization reduced the half-life of oil in wet forested soil in Alberta from normally 20 to 30 years to one year.*

## 2. Liming

*Microbial degradation of oil in soils with a low or highly alkaline pH can be enhanced by liming as most rapid oil degradation occurs at a near neutral pH (Ellis and Adams; 1961; Schwendinger, 1968; McGill and Nyborg; 1975). According to McGill (1978), if a site has been heavily fertilized, liming will benefit in the long run since there is a tendency for some fertilizers to acidify the soil.*

## 3. Organic Soil Conditioners

*Reports in the literature indicate that the sole use of organic ammendments such as peat, straw, sawdust, sugar or sewage sludge in reclaiming oil contaminated sites has little influence in hastening soil recovery (Kloke and Sahm, 1961; Kloke and Leh, 1963; Schwendinger, 1968; Loynachan, 1978; Dibble and Bartha, 1979).*

*Schwendinger (1968) reported that "the high C:N ratio of such materials simply aggravates the nitrogen deficiency originally created by the oil and that additions of carbon-rich materials would be the worst possible remedial action to take."*

*However, as there is a tendency for oiled soil to dry out, mixing uncontaminated soil, peat or feedlot manure with the contaminated soil may be beneficial in terms of improving the structure and moisture holding capacity of the soil (Schwendinger, 1968; McGill, 1978).*

## Microbial Seeding

Bacterial seeding has not been used very extensively in reclaiming oil contaminated sites. Schwendinger (1968) in a laboratory study, seeded oiled soil with a single species of bacteria (*Cellulomonas* sp) and found this to be effective at high levels of oil contamination. However, Jobson et al (1974) found only slight benefit in acceleration of oil decomposition from additions of a mixed culture of microorganisms (*Flavobacterium*, *Cytophaga*, *Pseudomonas*, *Xanthomonas*, *Alcaligenes*, and *Arthrobacter*) but reported some advantage in culturing the organisms on the oil to be degraded. Inoculations of more than $10^6$ cells per gram were considered necessary for any effective response.

Lehtomaki and Niemela (1975), in a laboratory study, applied brewery yeast to oil contaminated soil and reported that yeast, in different states of activity, provided useful nutrients for the decomposer organisms and enhanced the oil decomposition process. However, tests conducted by Dibble and Bartha (1979) failed to indicate any stimulation of oil biodegradation in soil by yeast supplementation.

McGill (1977) reported that the need for organisms to degrade oil is obvious but the need to add microbes to soil is subject to some controversy.

## 3. Burning

The advantages and disadvantages of burning off oil in contaminated soil have been summarized by McGill (1977). He bases his conclusions on work he and other researchers have conducted in Alberta.

*"Burning is often used as a final step in cleanup. The advantages of burning are that the last traces of free oil that cannot be picked up are disposed of and no obvious pools remain. Burning should also remove many of the volatiles from the crude, thus somewhat reducing the future toxicity of the oil. To the extent that burning accomplishes these ends, it is a valuable and useful technique.*

*The above advantages notwithstanding, burning also creates a number of additional problems. Five such problems may be listed:*

*(1)    The total amount of oil removed may be small. Results of a burning experiment conducted at our oil-spill plots at Redwater in 1974 indicate no significant difference in oil content between burned and unburned plots, one week after burning. Observations from previously burned field sites throughout Alberta indicate that burning in moss-covered areas or where oil could penetrate into the soil was generally not very effective in removing oil. In spots where the oil could not penetrate the soil, due to frost, water or an impermeable soil layer, burning appeared to be more effective.*

*(2)    Burning generally leaves a crust of unburned tarry residue on the surface. This crust prevents seed germination, will often seal the soil off and may prevent penetration through it*

*of shoots from any viable roots that may have survived the burn. For these reasons, burning usually requires a follow-up to break this crust before any success at site restoration can be expected on forest soils. In the past, burning was often considered the final step in cleanup. It was assumed that once the site was burned no oil would remain and the problem would be over. This is not the case in most of the burned spills I have seen.*

(3)     *Spreading of oil appears to result from some burns. This is most noticeable in the fringes of spills, where small fingers of oil may protrude from the center. A large, hot burn will not remove all the oil, but instead appears to heat the heavier ends enough to make them spread out from the fingers, thus increasing the affected area. DeBano et al (1970) report that burning also causes translocation of hydrophic substances down through soil. This may adversely affect water movement within the soil below the contaminated layer. Controlled burning could possibly prevent this, although controlling an oil spill burn is difficult.*

(4)     *Plants may be killed which would not have been killed by the oil in the soil. Oil in contact with the photosynthetic surface of plants will kill the tops, but not necessarily the roots. Burning, however, is likely to destroy many of the roots unless it is done in the winter and the amount of oil available on the surface to burn is small.*

*Observations reported by Hutchinson et al (1974) on burned and unburned portions of an oil spill in northern Alberta further support this conclusion. They found that revegetation was more rapid in the unburned portions of oil spill sites.*

(5) *During burning, some petroleum products may be only partially destroyed or rearranged by pyrolyis. These compounds can be toxic to animal life and may also be phyto-toxic."*

Another disadvantage which McGill didn't mention was air polluton which could further restrict the use of burning in a soil reclamation program.

Based on the literature, it would appear that the burning-off practice in restoring oil spill sites was more common in the past than it is today.

6. Plastic Sheeting

Gudin and Syratt (1975), found that placing a black polythene sheeting over oil contaminated soil enhanced oil degradation. They reported that rehabilitation of hydrocarbon contaminated sites should include covering with black polythene sheeting in winter to increase soil temperature. They also recommended covering dry areas in summer with transparent polythene to reduce water evaporation.

VII.  **Reclamation of Sub-Surface Soils**

1. Oxygenation

The reclamation of oil polluted subsoil is much more difficult than with surface soil since tillage as a means of improving aeration cannot be employed in most cases. Furthermore, it is generally accepted that subsoils are already slightly anaerobic and become even more oxygen deficient when polluted with oil. McGill (1977) outlined the benefits of forcing air into the subsoil. He reports "some definite advantage may result from pumping a stream of forced air through a perforated pipe installed at about 45-60 cm depth within the soil. This should help considerably in flushing out toxic volatiles and $H_2S$. In addition, it should increase the supply of $O_2$ at depths where slow $O_2$ diffusion into the soil limits oil decomposition."

On the basis of this information, oxygenating contaminated subsoil should benefit the oil biodegradation process.

2. Leaching with Nutrient and Detergent Solutions

According to Vanloocke et al (1975), the problem of amendments also is much more complicated than with surface soils since the nutrients not only have to migrate into the oil-water interphase, where oil biodegradation occurs, but also first have to reach these microsites where the latter interphases are fixed into the soil matrix. Nitrates are mobile in soil whereas phosphorus is not and Vanloocke et al (1975) have reported that active abatement of oil pollutants in deep soil layers will probably require the addition of mobile phosphorus compounds.

Lysimeter studies conducted by Vanloocke et al (1979) and others (DeBorger et al, 1974) indicate that elution with nutrient solutions of the polluted soil results in microbial activity or metabolites which enhance the desorption of oil components from the soil complex. They concluded that clean-up of sub-surface horizons polluted with oil is possible by intensive irrigation of the soil with a nutrient solution. They recommended using combinations of $NH_4NO_3$ + peptone and $NH_4NO_3 + ET_3PO_4$ for shallow and deep soil horizons, respectively.

They also advised that the soil percolate be pumped up and treated appropriately and further reported: "The clean-up procedure will require at least several months and at the best 10-20% of the oil adsorbed in the soil will be recovered. The remainder is either firmly bound to the soil or biodegraded. Nevertheless it continues to constitute a threat to the underlying water reserves."

Leaching of oil polluted soils with detergent solutions also has been reported to enhance hydrocarbon removal. Vanloocke et al (1975) reported that infiltrating detergents such as T-pol and Na-palmitate into the soil will enhance clean-up. Their conclusion was based on the work by Somers and Drak (1971) and Code and Swartz (1972).

## 3. Limitations

The major drawbacks of oxygenation and leaching subsoil with nutrient and detergent solutions are that these methods are both time consuming and expensive. Another drawback with leaching with detergents is the fact they may cause partial clogging of the soil (Somers and Drak, 1971; Emerson, 1974). Furthermore,

leaching methods increase the risk of potentially toxic hydrocarbons reaching the water table. On the basis of these concerns McGill (1977) reported that leaching of water soluble products as a means of reclaiming oil polluted subsoil should not be encouraged.

VII.    **Bioindicators and Revegetation**

As essential nutrients for plant growth are immobilized by oil decomposing soil microorganisms, it has been suggested that a revegetation program be delayed until there are reasonable assurances that nutrients are being mineralized by the soil (McGill and Nyborg, 1975).

Plants have been used extensively as bioindicators of oil residues in soil and overall site conditions. Simple germination tests and examining shoot or coleoptile length and overall appearance of indicator plants in reference to control plants, as well as regrowth or establishment of native vegetation on the site are useful criteria for assessing the stage of site recovery (Schwendinger, 1968; Rowell, 1975; Mitchell et al, 1979).

Raymond et al (1976) reported that nematodes also are good bioindicators of oil in soil as oil has nematicidal properties.

With respect to plants, many species have been found to be fairly tolerant of oil residues in soil after the toxic volatile fraction has been lost. Legumes and hardy grasses and weeds have been found to be fairly tolerant (Grummer, 1965; McGill and Nyborg; 1975).

McGill and Nyborg (1975) rated the ability of several plant species to survive under oil contaminated site conditions in Alberta. That work, presented earlier, clearly demonstrates that some plant species are better than others for use in a revegetation program.

When a spill site has recovered to the extent that a desired plant stand will grow and yield as favourably as corresponding plants in unaffected neighbouring areas or in control plots, it is considered to be reclaimed (McGill, 1978).

IX.    **Summary and Conclusions**

In summary, oil spills on land can adversely affect existing vegetation, drastically alter plant community relationships and contaminate the soil altering its physical and chemical properties to the extent that it becomes unsuitable for plant growth.

The most adverse effects of oil polluted soil on vegetation, aside from any direct toxicity, would appear to be interference with nutrient supply through microbial immobilization and with water-plant-soil relations. Reducing or anaerobic conditions which can result in the soil following an oil spill also can increase the solubilization of manganese and iron which can be toxic to plants.

Microbial degradation and volatilization are the principal mechanisms by which oil in soil is decomposed. In the case of microbial degradation, aerobic decomposing organisms appear to play a greater role than their anaerobic counterparts.

Laboratory studies have revealed that paraffins in oils are the least toxic and most rapidly metabolized by hydrocarbon decomposing organisms compared to aromatics, olefins and napthenes. However, based on field studies with various oils, it has been shown that a high paraffinic fraction in oil does not always confer a high biodegradation rate under field conditions. Based on

*the literature, it would appear that oil properties resulting in inaccessability to organisms (high viscosity, insolubility) and a high content of complex asphaltic material will retard decomposition the most. Additives in refined oils also can prevent rapid oil degradation in soils.*

*Several environmental factors such as climatic and site conditions, soil type, organic matter and moisture content of the soil, also can influence the amount of oil retained by the site and affect the rate of oil biodegrdation.*

*In reclaiming oil polluted surface soils in temperate climates, most experimental studies indicate that tillage and fertilization should be emphasized. Maintaining a near neutral soil pH through liming, maintaining adequate soil moisture and air temperatures (12 to 30 C) also should provide an environmnent conducive to rapid microbial activity and hence reduce the restoration time. Covering the oil spill site with black polythene sheeting in the winter to increase soil temperature and covering dry areas in summer with transparent polythene to reduce water evaporation also has been found to be beneficial. As there is a tendency for oiled soils to dry out and for their structure to deteriorate, the addition of straw or manure also can benefit by improving structure and moisture holding capacity of the soil.*

*The site itself and the extent of downward migration of oil into the soil profile will largely influence the type of reclamation program. On a wet, poorly drained site, draining off the surface water or burning likely would precede any of the above practices. In addition, at sites where the subsoil has been contaminated, forcing air through perforated pipes placed deep in the soil or irrigating the subsoil with nutrient or detergent solutions to enhance restoration may be the only options.*

Restoring a site to the point where it will support a desired plant species or plant community is the ultimate objective of a reclamation program. It has been recommended that an extensive revegetation program should be delayed until there are reasonable assurances that nutrients essential for plant growth are being mineralized by the soil since plants compete with oil decomposing organisms for available soil nutrients.

Plants and nematodes have been used as bioindicators of oil presence in soil and provide useful criteria for assessing the stage of site recovery.

With respect to types of vegetation best suited for use in a reclamation program, legumes and hardy grasses appear most desirable. However, the type of revegetation program is largely dependent on the site and climatic conditions.

In conclusion, site conditions are seldom optimum for plant growth following an oil spill. The oil decomposition process is largely dependent on soil microorganisms and proceeds fastest under aerobic conditions. Thus, by providing an environment conducive to rapid microbial activity with emphasis on maintaining good aeration, adequate nutrients and a near neutral soil pH, the time to restore oil contaminated soils can be markedly reduced particularly in temperate climates.

X. **References**

Anderson, J.W., Neff, J.M., Cox, B.A., Tatem, N.E. and G.M. Hightower. 1974. Characteristics of dispersions and water-soluble extracts of crude and refined oils and their toxicity to estuarine crustacea and fish. Mar. Biol. 27:75.

Atlas, R.M. 1977. Stimulated petroleum biodegradation. Crit. Rev. Microbiol. 5:371-386

Badger, G.W. 1948. The carcinogenic hydrocarbons chemical constitution and carcinogenic activity. Brit. J. Cancer 2: 309-350.

Baker, J.M. 1969. The effects of oil pollution and cleaning on salt marsh ecology. Field Studies Council, Orielton Field Centre, Annual Report, pp 3-26.

Baker, J.M. 1970. The effects of oils on plants, Environ. Pollut. 1:27-44.

Baker, J.M. 1971. Seasonal effects of oil pollution on salt marsh vegetation. OIKOS 22:106-110.

Bartha, R. and R.M. Atlas. 1977. The microbiology of aquatic oil spills. Adv. Apl. Microbiol. 22:225-266.

Blankenship, D.W., and R.A. Larson. 1978. Plant growth inhibition by the water-extract of crude oil. Water, Air and Soil Poll. 10:471-476.

Blumer, M. 1971. Scientific aspects of the oil spill problem. Environmental Affairs. 54-73. (Reprinted in Nato 1970).

Boylan, D.B., and B.W. Tripp. 1971. Determination of hydrocarbons in seawater extracts of crude oil and crude oil fractions. Nature 230:44-47.

Boyles, D.T. 1967. M.Sc. Thesis, Department of Botany (Plant Physiology). Imperial College, University of London, London, England.

Brunnock, J.V., Duckworth, D.F. and G.G. Stephens. 1968. Analysis of beach pollutants. In: Scientific Aspects of Pollution of the Sea by Oil. P. Hepple, ed., Institute of Petroleum, London. pp. 12-27.

Carr, R.H. 1919. Vegetative growth in soils containing crude petroleum. Soil Sci. 8:67-68.

Carruthers, W., Stewart, H.N.W. and D.A.M. Watkins. 1967. 1, 2-benzanthracene derivatives in a kuwait mineral oil. Nature 213: 691-692.

Cowell, E.G. 1971. Oil pollution in perspective. In: The Ecological Effects of Oil Pollution on Littoral Communities, E.B. Cowell (Ed.). Proceed. Sympos. Nov. 30 - Dec. 1, 1970, sponsored by Institute of Petroleum, 61 Cavendish Street, London, WIM 8AR. Elsevier Publishing Co. Ltd., London, pp. 224-234.

Crafts, A.S. and H.G. Reiber. 1948. Herbicidal properties of oils. Hilgardia 18:77-156.

Curl, H., Jr., and K. O'Connell. 1977. Chemical and physical properties of refined petroleum products. NOAA Tech. Memo. ERL MESA-17. Boulder, Colo. pp. 1-35.

Currier, H.G. 1951. Herbicidal properties of benzene and certain methyl derivatives. Hilgardia 20:383-406.

Currier, H.B. and S.A. Peoples. 1954. Phytotoxicity of hydrocarbons. Hilgardia 23:155-173.

DeBano, L.F., Mann, L.D., and D.A. Hamilton. 1970. Soil Sci. Soc. Amer. Proc. 34:130-133.

DeBorger, R., Jacobs, T., Pijck, J., Vanloocke, R., Verlinde, A., Verstraete, W. and J.P. Voets. 1974. "Belgian national R and D program on the environment - Groundwater pollution - Annual report 1974" (offices of the Prime Minister - Ministry of Science Policy Programming).

DeJong, E. 1980. The Effect of a crude oil spill on cereals, Environ. Pollut. 22:187-196.

Dibble, J.T., and R. Bartha. 1979. Leaching aspects of oil sludge biodegradation in soil. Soil Sci. 127:365-370.

Dietz, D.N. 1972. Behavior of components from spilled oil on their way through the soil. Paper SPE 4077, SPE-AIME 47th Metg S. Antonio, Tex.

EcKart, R.E. 1967. Cancer prevention in the petroleum industry, Int. J. Cancer 3:656-661.

Ellis, R., Jr. and R.S. Adams. 1961. Contamination of soils by petroleum hydrocarbons. Advan. Agron. 16:197-216.

Emerson, W.W. 1974. The flow of sodium alkylbenzene sulfonate through porous media. Intern. J. Envir. Pollut. 7:39-52.

Fedorak K, P.M. and D.W.S. Westlake. 1981. Degradation of aromatics and saturates in crude oil by soil enrichments. Water, Air and Soil Pollut. 16:367-375.

Floodgate, G.T. 1972. Microbial degradation of oil. Mar. Poll. Bull., 3:41-43.

Frank, C.E. 1950. Hydrocarbon autoxidation. Chem. Rev. 46:155-169.

Franke, H.C. and F.E. Clark. 1974. Disposal of oil wastes by microbial assimilation. U.S. Atomic Energy Report Y. 1974. Washington, D.C. pp. 45.

Frankenberger, W.T., Jr. and J.B. Johanson. 1982. J. Environ. Qual. 11:602-607.

Freedman, W. and T.C. Hutchinson. 1976. Physical and biological effects of experimental crude oil spills on low arctic tundra in the vicinity of Tuktoyaktut, N.W.T. Canada. Can. J. Bot. 54:2219-2230.

Garner, J.H. 1971. Changes in soil and death of woody ornamentals associated with leaking natural gas. Phytopathology 61:892.

Giddens, J. 1976. Spent motor oil effects on soil and crops. J. Environ. Qual. 5:179-181.

Ginsburgh, J.M. 1931. Penetration of petroleum oils into plant tissues. J. Agr. Res. 43:459-474.

Gode, P. and W. Schwartz. 1972. Untersuchungen zur Erdolmikrobiologie. Z. Ellg. Mikrobial. 12:631-635.

Gossen, R. and D. Parkinson. 1973. Microbiological Investigations of crude oil inundated arctic soils, In: Oil and the Canadian Environment, D. MacKay and W. Harrison (Eds), Proceedings of the Conference sponsored by the Institute of Environmental Sciences and Engineering, University of Toronto. pp. 56-58.

Graef, W. and C. Winter. 1968. 3, 4-benzopyrene in Erdoel. Arch. Hyg. 152:289-293.

Grummer, H.J. 1965. Investigations on sandy soil flooded by crude oil in Emsland. Landwirtsch. Forsch. 17:229-243.

Gruse, W.A. 1967. Motor fuels. Reinhold Publishing Corp., N.Y.

Guard, N.E., Hunter, L. and L.H. DiSalva. 1975. Identification of potential biological effects of the major components in the seawater extract of a Bunker Fuel. Bull. Environ. Contam. and Toxicol. 14:395-400.

Gudin, C. and W.S. Syratt. 1975. Biological aspects of land rehabilitation following hydrocarbon contamination. Environ. Pollut. 8:107-112.

Gunkel, W. 1968. Bacteriological investigations of oil polluted sediments from the cornish coast following the "Torey Canyon" disaster, Fld. Stud. 2:151-158.

Guseinov, D.M., and Asadov, S.D. 1958. Akad. Nauk. Azerbaidzhan SSR. 14:1015-1019, Chem Abstr. 53:10633.

Harris, J.O. Petroleum Wastes in the Soil (on file).

Havis, J.R., Dallyn, S. and R.D. Sweet. 1950. Herbicidal properties of petroleum hydrocarbons. American Chemical Society Symposium. "The Agricultural Application of Petroleum Products, Washington, pp. 105-113.

Hill, J.B. and J.G. Moxey, Jr. 1960. Gasoline. In: Petroleum Products Handbook. V.B. Guthrie (ed.) McGraw-Hill Book Co., N.Y. pp. 4-1-4-54.

Hubbard, E.H.  Fate and effects of oil on land and in fresh waters (on file).

Huseinov, D.M.  1960.  Trans 7th Int. Congr. Soil Sci.  3:253-259.

Hutchinson, T.C. and J.A. Hellebust.  1974.  Oil spills and vegetation at Normal Wells, N.,W.T. Environmental-Social Program.  Northern Pipelines Task Force, Ottawa, Information Canada Report 73-43. pp. 129.

James, W.S.  1960.  Lubricating oils and gases.  In:  Petroleum products handbook.  V.B. Guthrie (ed.) McGraw-Hill Book Co., N.Y. p.  9-1-9-141.

Jensen, V.  1975(a).  Decomposition of oily wastes in soil.  Proc. 1st Int.  Conf. Biodegradation Humification, Nancy, 1974.  pp. 278-287.

Jensen, V.  1975(b).  Bacterial flora of soil after application of oily waste.  Oikos.  26:152-158.

Jobson, A., Cook, F.D. and D.W.S. Westlake.  1972.  Microbial utilization of crude oil.  Appl. Microb.  23:1082-1089.

Jobson, A., McLaughlin, M., Cook, F.D., and D.W.S. Westlake.  1974. Effect of amendments on the microbial utilization of oil applied to soil.  Appl. Microb. 27:166-171.

Johnston, R.  1970.  The decomposition of crude oil residues in sand columns.  J. Mar. Biol. Ass.  50:925-937.

Jones, J.G. and M.A. Edington.  1968.  An ecological survey of hydrocarbon-oxidizing micro-organisms.  J. Gen. Microb.  52:381-390.

Kaczmarek, T.D. 1981. Bioassay and chemical analysis for hazardous materials in residual oils. Volume 2. EPA -600/7-81-080B. Appendices. (Final rept. Jun 77 - Jun 80). Westinghouse Research and Development Centre, Pittsburgh, Pa. pp. 477.

Kalichevsky, V.A. and E.N. Peters. 1960. The raw material crude petroleum and natural gas. In: Petroleum products handbook. B. Guthrie (ed.) McGraw-Hill Book Co., N.Y. pp. 1-1-1-39.

Kennaway, E.L. 1924. Cancer-producing tars-and tar fractions. J. Industr. Hygiene 5:462-488.

Kinako, P.D.S. 1981. Short-term effects of oil pollution on species numbers and productivity of a simple terrestrial ecosystem. Environ. Pollut. 26:87-91.

Kincannon, C.B. 1972. Oily waste disposal by soil cultivation process. U.S. Environmental Prot. Agency. Environ. Prot. Tech. Ser. EPA - R2-72-110.

Kloke, A. and H.O. Leh. 1963. Nachr Bl. dtsch. PflSchDienst Stuttgart. 15:85-88.

Kloke, A. and U. Sahm. 1961. Nachr Bl. dtsch. PflSchDienst Stuttgart. 13:124-126.

Knight, H., Chamberlain, H.C. and C.D. Samuels. 1929. Limiting factors in the use of saturated petroleum oils as insecticides. Plant Phys. 4:299-321.

Lachman, W.H. 1944. The use of oil sprays as selective herbicides for carrots and parsnips. Proc. Am. Soc. Hort. Sci. 45:445-448.

Larson, C.M., and R. Larson. 1960. Additives for petroleum products. In: Petroleum products handbook. V.B. Guthrie (ed) McGraw-Hill Book Co. N.Y. pp 2-1-2-48.

Laville, E. 1963. Contribution a l'etude de la penetration et la localisation des huilles dans la feuille de bananier. Fruits 18:339-344.

Lehtomaki, M. and S. Niemela. 1975. Improving microbial degradation of oil in soil. Ambio 4:126-129.

Leonard, O.A. and V.C. Harris. 1952. The effects of aliphatic hydrocarbons on the hypocotyls of cotton and soybeans and on the shoots of nutgrass, Johnson grass, and other weeds by the directional spray technique. Weeds 1:256-273.

Lewis, F.J. 1945. Physical conditions of the surface of the mesophyll cell walls of the leaf. Nature 156:407-409.

Llanos, C. and A. Koller. 1976. Changes in the flora of soil fungi following oil waste application. OIKOS 27:377-382.

Loynachan, T.E. 1978. Low-temperature mineralization of crude oil in soil. J. Environ. Qual. 7:494-500.

MacKay, D., Charles, M.E. and C.R. Phillips. 1972. The physical aspects of crude oil spills on northern terrains. An interim report to the Arctic Land Use Research Program of the Department of Indian and Northern Affairs, Ottawa.

Malina, J.F. 1964. Toxicity of petrochemicals in the aquatic environment. Water and Sewage Works 111:456-460.

McCown, D.D. and F.J. Deneke. 1973. Plant germination and seedling growth as affected by the presence of crude petroleum. In Proc. Symp. on Impact of Oil Resour. Dev. on Northern Plant Communities, B.H. McCown and D.R. Simpson (ed). 23rd AAAS Alaskan Sci. Conf., Aug. 17, 1972, University of Alaska, Fairbanks. Occas. Pub. on Northern Life No. 1, Inst. of Arctic Biol., Univ. of 'Alaska. p. 44-51.

McGill, W.B. 1977. Soil Restoration following oil spills - a review, J. of Can. Petrol. Techn. April-June: 60-67.

McGill, W.B. 1978. Oil spills. Crops and Soils Magazine, pp. 6-9.

McGill W.B. 1980. Factors affecting oil degradation rates in soils In: Disposal of Industrial and Oily Sludges by Land Cultivation, D.M. Shilesky (ed.), Resource Systems and Management Association, Northfield, New Jersey, pp 103-122.

McGill, W.D. and M. Nyborg. 1975. Reclamation of wet forest soils subjected to oil spills. Alberta Inst. Pedol. Pub. No. G-75-1. pp. 129.

Minshall, W.H. and C.A. Helson. 1949. The herbicidal action of oils. Proc. Am. Soc. Hort. 53:294-298.

Mitchell, W.W., Loynachan, T.E. and K.J.D. McKendrick. 1979. Effects of tillage and fertilization on persistence of crude oil contamination in an Alaskan soil. J. Environ. Qual. 8:525-532.

Nagata, T. and K. Muramatsic. 1968. Soil Sci. Plant Nutr. 14:208.

Nelson, W.L. 1958. Petroleum refinery engineering. 4th ed. McGraw-Hill Book Co., N.Y.

Nelson-Smith, A. 1970. The problem of oil pollution of the sea. Adv. Mar. Biol. 8:215-306.

ODU, C.I.I. 1972. Microbiology of soils contaminated with petroleum hydrocarbons. I. Extent of contamination and some soil and microbial properties after contamination. J. Inst. of Petrol. 58:201-208.

Ottway, S. 1971. The comparative toxicities of crude oils. In: The Ecological Effects of Oil Pollution on Littoral Communities. E.B. Cowell (ed.). Proceedings of Symposium, Nov. 30 - Dec. 1, 1970, sponsored by Institute of Petroleum, 61 New Cavendish Street, London, W1M 8A4. Elsevier Publishing Co. Ltd., London. pp. 172-180.

Plice, M.J. 1948. Some effects of crude petroleum on soil fertility. Proc. Soil Sci. Soc. Amer. 13:413-416.

Raisbeck, J.M. and M.E. Mohtadi. 1974. The environmental impacts of oil spills on land in the arctic regions. Water, Air and Soil Pollut. 3:195-208.

Raymond, R.L., Hudson, J.O. and V.W. Jamison. 1976. Oil degradation in soil. Appl. and Env. Microb. 31:522-535.

Rohrbaugh, P.W. 1941. Physiological effects of petroleum oil sprays on citrus. J. Econ. Entomol. 34:812-815.

Rowell, M.J. 1975. Restoration of soil spills on agricultural soils. In: Proc. conf. The Environmental Effects of Oil and Salt Water Spills on Land. Alberta Environmnent Research Secretariat, Edmonton, 1975. pp. 250-276.

Rowell, M.J. 1980. Land cultivation in cold regions. In: Disposal of Industrial and Oily Sludges by Land Cultivation, D.M. Shilesky (ed.) Resources Systems and Management Association, Northfield, New Jersey. pp. 103-122.

Schwendinger, R.B. 1968. Reclamation of soil contaminated with oil. J. Inst. of Petrol. 54:182-197.

Somers, J.A. and J. Drak. 1971. "Bodemverontreiniging door olie. Mobilisering van immobiele olieresten in de bodem" IG-TNO werkrapport A59.

Speers, G.C. and E.V. Whitehead. 1969. Crude Petroleum. In: Organic Geochemistry, Eglinton G. and M.R.J. Murphy (Ed). Springer, Berlin, pp. 638-675.

Toogood, J.A. 1974. Effect of light oil spills on crop growth. In: Workshop on Reclamation of disturbed lands in Alberta, Edmonton, Alta. Proceedings edited by D. Hocking and W.R. MacDonald. Edmonton, Alta, Northern Forest Research Centre (Northern Forest Research Centre Information Report NOR-X-116). pp. 102-105.

Toogood, J.A. and W.B. McGill. 1977. The reclamation of agricultural soils after oil spills. Part 2. Extension, Alberta Inst. Pedol. No. M-77-11. 45 p.

Treccani, V. 1965. Microbial degradation by aliphatic and aromatic hydrocarbons. Z. Allg. Mikrobial. 5:332-341.

Udo, E.J. and A.A.A. Fayemi. 1975. The effect of oil pollution of soil on germination, growth and nutrient uptake of corn. J. Environ. Qual. 4:537-540.

Vanloocke, R., DeBorger, R., Voets, J.P. and W. Verstraete. 1975. Soil and groundwater contamination by oil spills; problems and remedies. Int. J. Environ. Stud. 8:99-111.

Vanloocke, R., Verlinde, A.M. and W. Verstraete. 1979. Microbial release of oil from soil columns. Environ. Sci. and Tech. 13:346-348.

VanOverbeek, J. and R. Blondeau. 1954. Mode of action of phytotoxic oils. Weeds 3:55-65.

Volk, V.V. 1980. Oily waste and plant growth. In: Disposal of Industrial and Oily Sludges by Land cultivation, D.M. Shilesky (ed), Resource Systems and Management Association, Northfield, New Jersey, pp. 123-138.

Walker, J.D., Cafone, L., Jr. and J.J. Cooney. 1973. Microbial petroleum degradation: The role of Gladosporium resinae. In: Proceedings of Joint Conference on Prevention and Control of Oil Spills, March 13-15, 1973, Washington, D.C. Sponsored by American Petroleum Institute, Environmental Protection Agency, and the United States Coast Guard, pp. 821-825.

Walker, J.D., Seasman, P.A. and R.R. Colwell. 1975. Effect of S. Louisiana crude oil and No. 2 fuel oil on growth of heterotrophic microorganisms. Env. Pollut. 9:15-33.

Walker, J.D., Colwell, R.R. and L. Petrakis. 1976. Biodegradation rates of components of petroleum. Can. J. Microb. 22:1209-1213.

Walker, J.D., Petrakis, L. and R.R. Colwell. 1976. Comparison of the biodegradability of crude and fuel oils. Can. J. Microb. 22:598-602.

Watts, J.R., Corey, J.C. and K.W. McLeod. 1982. Land application studies of industrial waste oils. Environ. Pollut. 28:165-175.

Westlake, D.W.S., Jobson, A., Phillippe, R. and F.D. Cook. 1974. Biodegradability and crude oil composition. Can. J. Microb. 20:915-938.

Whittemore, I.M. 1979. High resolution gas chromatography of the gasolines and napthas. In: Chromatography in petroleum analysis. K.N. Altgett and T.H. Goun (ed) Marcel Dekker Inc. N.Y. pp. 41-74.

Wilson, J.M. and D.M. Griffin. 1975. Water potential and the respiration of microorganisms in the soil. Soil Biol. Biochem. 7:199-204.

Winters, K., O'Donnel, R., Batterson, J.C., and C. Van Baalen. 1976. Mar. Biol. 36: 269.

Young, P.H. 1935. Oil mass theory of petroleum oil penetration into protoplasm - Am. J. Bot. 22:1-8.

Zobell, C.E. 1950. Assimilation of hydrocarbons by microorganisms. Advances in Enzymology. 10:443-486.

Zobell, C.D. 1962. The occurrence, effects and fate of oil polluting the sea. Int. J. Air, Wat. Pollut. 7:173-198.

Zuidema, H.H. 1959. The performance of lubricating oils. Reinhold Publishing Corp. N.Y.

RNE/hm

PH/34/1